ELECTRON PARAMAGNETIC RESONANCE STUDIES OF A VISCOUS NEMATIC LIQUID CRYSTAL - EVIDENCE COUNTER TO A SECOND-ORDER PHASE CHANGE

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16. Abstract

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SUMMARY

The ordering in a viscous nematic liquid crystal was studied using vanadyl acetyl-acetonate (VAAC) and several nitroxides as paramagnetic probes. The ordering curve for VAAC at both K-band and X-band shows a slope discontinuity at a reduced temperature of 0.85. This discontinuity is caused by the tumbling time of the VAAC becoming comparable with the hyperfine splitting. The slope discontinuity is not present in the ordering curves of the nitroxides. The results are taken as evidence counter to the presence of a second-order phase transition.

INTRODUCTION

Previously, we have studied the ordering of several nematic liquid crystals using vanadyl acetylacetonate (VAAC) as a paramagnetic probe (ref. 1). One liquid crystal (ref. 2), bis(4'-n-octyloxybenzal)-2-chloro-1, 4-phenylenediamine (BOCP), is particularly interesting because of the viscous effects it displays over its extermely long nematic range (ref. 3). The ordering of VAAC dissolved in BOCP was studied as a function of temperature, and a discontinuity in slope was observed at a reduced temperature T* of 0.85 (where T* is the ratio of the temperature in kelvins to the clearing temperature in kelvins). We have attributed this discontinuity to an inhibition of the probe's tumbling due to increased viscous effects. Other authors' (ref. 4) have suggested the possibility that a second-order phase change might be responsible for a sharp increase

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in viscosity at $T^* = 0.85$ and, hence, account directly for the discontinuity in the slope of the ordering curve.

In an effort to clarify this point we have performed additional experiments at both X-band ($\approx 10^{10}$ Hz) and K-band ($\approx 2.5 \times 10^{10}$ Hz) using both VAAC and nitroxide probes. Although these experiments are not conclusive, they are helpful in determining whether a second-order phase transition is present at $T^* = 0.85$. They also demonstrate that the hyperfine splitting sets the tumbling time scale for the experiment.

This study is part of a continuing cooperative research program between the personnel of NASA Lewis Research Center and Kent State University. The research in the Liquid Crystal Institute at Kent State University is partly supported by AFOSR contract F 44620-69-C-0021 and NSF contract GH-34164X.

DESCRIPTION OF EXPERIMENT

The nematic range of BOCP as reported by Arora et al. (ref. 3) is 59° to 179° C. BOCP was doped ($\sim 10^{-3}$ M) with either VAAC or one of several nitroxide probes that are described below.

In figure 1 the structures of the nitroxide probes used in this study are shown. All of these nitroxides are methyl protected except nitroxide 4.

Nitroxides 1 and 2 were prepared according to the method of Briere, Remaire, and Rasset (ref. 5) and then purified by sublimation at 0.5 millimeter and 70° C. These nitroxides were not ordered by the liquid crystal because of their small size. Nitroxide 3 was prepared according to the method of Rozantsev (ref. 6). It was ordered by the liquid crystal, but this nitroxide decomposed above 140° C. Nitroxide 4 was prepared according to the method of Bruce (ref. 7). Its large size inhibited its freedom of tumbling, so that its spectra is characteristic of a spatial rather than a temporal average (ref. 2).

Nitroxide 5 was prepared by the reaction of 0.3 gram (1.7×10^{-3} mole) nitroxide 2 with 0.47 gram (1.7×10^{-3} mole) para-n-octyloxybenzoylchloride in 5 milliliters dry pyridine. The solution was stirred for 24 hours and then poured onto ice water, filtered, and dried. The material was recrystallized from hexane to give rose colored crystals whose melting point was 50° to 52° C. This nitroxide was ordered only slightly by the liquid crystal but decomposed at temperatures above 120° C.

Nitroxide 6 was prepared by mixing 0.2 gram (1.16×10^{-3} mole) of nitroxide 2 with 0.25 gram (1.2×10^{-3} mole) of para-nitro cinnemylchloride in 5 milliliters dry pyridine. After stirring for 36 hours the material was filtered and dried; it was then recrystallized from ethyl acetate/hexane to give rose colored crystals which melted at 150° to

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152° C. Nitroxide 6 was ordered by the liquid crystal and showed no signs of decomposition up to 200° C.

The X-band paramagnetic resonance spectra (EPR) were obtained using a modified Varian E-12 spectrometer and a modified Varian 4547 variable temperature accessory. The sample temperature was measured by a 36-gage copper-constantan thermocouple inserted in the nitrogen stream that heated the sample.

The K-band EPR spectrometer built at Kent State University employs a modified Pound automatic frequency control to stabilize the klystron frequency and a balanced bolometer bridge detection system. The entire sample cavity was heated by a chromel heater cemented to the cavity, and the temperature was monitored by a 36-gage copper-constantan thermocouple cemented to the cavity. The details of our temperature controller are reported elsewhere (ref. 8).

THEORY

The structure and properties of VAAC have been previously described (refs. 1 and 2). It has axial "g" and hyperfine tensors, so its Hamiltonian may be written as

$$\mathscr{H} = \beta\left[g_{\parallel}H_r S_r + g_{\perp}(H_p S_p + H_q S_q)\right] + A_{\parallel}I_r S_r + A_{\perp}(I_p S_p + I_q S_q) \tag{1}$$

where p, q, and r are a set of coordinate axes fixed to the VAAC molecule with the r-axis parallel to the V = 0 bond direction. Following the development of reference 2, we find that lines corresponding to different values of the azimuthal component of the nuclear spin m_I are predicted at magnetic field positions (refs. 8 and 9),

$$H = \left(\frac{2}{g}\right)H_0 - \left(a + \frac{2b}{3}\sigma_z\right)m_I - \frac{\left(a - \frac{b}{3}\sigma_z\right)^2}{2H_0}\left[I(I + 1) - m_I^2\right] \tag{2}$$

where H_0 corresponds to the magnetic field for g = 2, a is the isotropic portion of the hyperfine tensor (-1.07×10^{-2} T or -107 G), and b is the anisotropic portion of the hyperfine tensor (-1.21×10^{-2} T). The ordering parameter σ_z, is defined as $\langle 3\cos^2\theta - 1\rangle/2$. Consider any two lines whose m_I values are α and β, respectively. Then the separation (in tesla) between these two lines is

$$H_\beta - H_\alpha = (\alpha - \beta)\left(a + \frac{2b}{3}\sigma_z\right) - (\alpha^2 - \beta^2)\frac{\left(a - \frac{b}{3}\sigma_z\right)^2}{2H_0} \tag{3}$$

If $\alpha = -\beta$, then the second-order term becomes zero and the ordering parameter is easily calculated to be

$$\sigma_z = \frac{3}{2b}\left(\frac{H_\beta - H_{-\beta}}{2\beta} + a\right) = \frac{3}{2b}(\langle a \rangle + a) \tag{4}$$

where $\langle a \rangle$ is the average experimental hyperfine splitting. If $\alpha \neq -\beta$, then second-order terms must be retained, and the corresponding expression for the ordering parameter is considerably more complicated. The K-band data required us to use the splitting between the -7/2 line and the -1/2 line, and the expression for the ordering parameter in terms of $\Delta H = H_{-1/2} - H_{-7/2}$ is given by

$$\sigma_z = \frac{3H_0}{2b}\left(\frac{2a}{H_0} - 1 + \sqrt{1 - \frac{6a}{H_0} - \frac{2\,\Delta H}{3H_0}}\right) \tag{5}$$

The nitroxide probes used in our experiment have axial hyperfine tensors, nuclear spins of 1 and electronic spins of 1/2 yielding three line EPR spectra. The isotropic portion of the hyperfine splitting $a = 1/3(A_\parallel + 2A_\perp)$ is obtained from the spectrum of the probe when the host is in the isotropic phase. In the case of methyl protected nitroxides (ref. 10), $A_\perp = 0.188\,A_\parallel$, so we can calculate $A_\parallel$, $A_\perp$, and $b = A_\parallel - A_\perp$. For the case under discussion $a \cong 1.5\times10^{-3}$ tesla, $b \cong 2.66\times10^{-3}$ tesla, $A_\parallel \cong 3.28\times10^{-3}$ tesla, and $A_\perp \cong 6.2\times10^{-4}$ tesla. These values are used in equation (4) to calculate the ordering of the nitroxide probe.

It is also possible to calculate the nitroxide tumbling times from the line widths and heights. The expression relating these quantities is (ref. 11)

$$\tau_c = \frac{2.37\times10^{-6}\,W(o)}{H}\left[\left(\frac{h_1}{h_o}\right)^{1/2} - \left(\frac{h_{-1}}{h_o}\right)^{1/2}\right] \tag{6}$$

where $W(o)$ is the peak-to-peak width of centerline ($m_I = 0$) in tesla, H is the magnetic field, and h_m is the height of the m_I^{th} line.

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RESULTS

We have measured the ordering of VAAC dissolved in BOCP against reduced temperature at K-band. The low field line of the K-band spectrum is largest, and the line amplitudes decrease monotonically as the field is increased (ref. 8). This effect has also been observed for VAAC dissolved in an isotropic liquid (refs. 12 and 13). Because of this effect and the poor signal to noise ratio of the K-band spectrometer, the last four lines of the spectra were often lost in the noise. Therefore, we used the first four lines to calculate the order parameter, taking into account the second-order terms, as described in the THEORY section. Equation (5) was used to calculate the ordering parameter.

The ordering parameter of VAAC in BOCP against reduced temperature at K-band appears in figure 2(a). In figure 2(b) we show the corresponding curve obtained at X-band as previously reported (ref. 2). Both curves are approximately the same shape, displaying a discontinuity in slope at T* = 0.85. This correspondence indicates that the temperature at which the discontinuity occurs is independent of the spectrometer frequency.

We have also obtained the spectra of nitroxide probes 3 and 6 at both K-band and X-band. The symmetric line shape of the spectra indicate that these probes are tumbling rapidly. The experimental hyperfine splitting can be used to calculate the ordering of the nitroxide molecule as indicated in the THEORY section. Because the second-order terms are not important for this case, equation (4) is used for these calculations.

The ordering parameter of nitroxide 3 calculated from the K-band and X-band data is shown in figure 3. Similar results were obtained using nitroxide 6. There is no indication of a slope discontinuity on either curve.

Figure 4 shows the tumbling times for nitroxides 3 and 6 as calculated using equation (6). The values obtained at the different frequencies show good agreement. There is no indication of a slope discontinuity on any of these curves. Nitroxide 6 tumbles more slowly than 3 due to its larger size.

DISCUSSION

The slope discontinuity in the ordering parameter curve at a reduced temperature of 0.85 has been explained as resulting from an increase in the viscosity. If a second-order phase transition occurred at this temperature, it could be accompanied by a sharp increase in the viscosity of the liquid crystal, and this would result in an apparent increase in the order, as was observed experimentally. However, our results with ni-

troxide probes do not indicate any sharp rise in viscosity. This is especially true of the results of tumbling time against temperature (fig. 4).

Our results with VAAC at the two different frequencies (X-band and K-band) indicate that the Larmor frequency has no effect on the ordering parameter. The obvious alternative is that the hyperfine splitting is the important quantity that sets the temporal scale in these experiments. Actually, it is not necessary to have a sharp rise in the viscosity at $T^* = 0.85$ to explain the slope discontinuity in the ordering parameter. We propose that, when the tumbling time becomes comparable with the hyperfine split ting, there is an abrupt contraction of the spectra indicating a sharp increase in apparent order. The fact that the ordering parameter curves for the nitroxide probes do not show any discontinuity is in agreement with this explanation because the hyperfine splitting of the nitroxides is much less than that of the VAAC: 1.5×10^{-3} T ($\tau = 5 \times 10^{-7}$ sec) compared with 1.07×10^2 T ($\tau = 3 \times 10^{-8}$ sec).

Our computer calculated spectra (ref. 14) of VAAC dissolved in a viscous liquid crystal confirm this explanation. The results of these calculations show that the ordering parameter is independent of tumbling time until the tumbling time is reduced to a value near the hyperfine splitting (about two or three times greater). With further decrease of tumbling time, the spectra contract rapidly. For tumbling times equal to or less than the hyperfine splitting, the apparent order is determined solely by the tumbling time and is independent of the real order in the liquid crystal.

In conclusion, we have shown that the abrupt rise in the ordering parameter of BOCP at a reduced temperature of 0.85 can be adequately explained without assuming the occurrence of a second-order phase transition. In addition, our results with nitroxide probes contraindicate a phase transition since neither the order of the liquid crystal nor the tumbling time of the probes display any discontinuities at this temperature.

Lewis Research Center,
    National Aeronautics and Space Administration,
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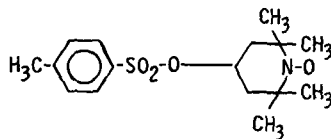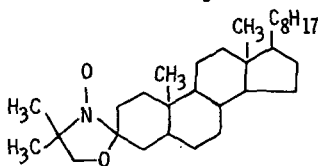
1. 3-pyrrolin-1-oxyl, 3 carbamyl-2, 2, 5, 5 tetramethyl.
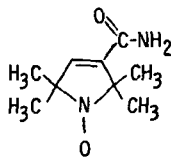
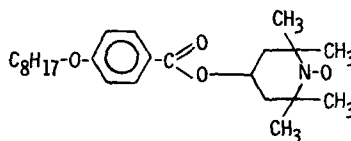2. Piperdinooxy-4-hydroxy-2, 2, 6, 6-tetramethyl.
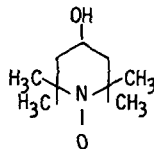
3. Piperdinooxy-4-hydroxy-2, 2, 6, 6-tetramethyl, p-toluene sulfonate.

4. Spiro [sα-cholestane-3, 2'-oxazolidin]-3'-yloxy, 4, 4'dimethyl.

5. Piperdinooxy-4-hydroxy 2, 2, 6, 6-tetramethyl p-n-octyloxybenzoate.

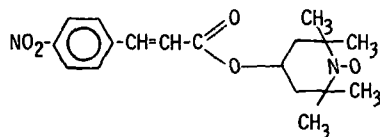6. Piperdinooxy-4-hydroxy 2, 2, 6, 6-tetramethyl p-nitrocinnimate.

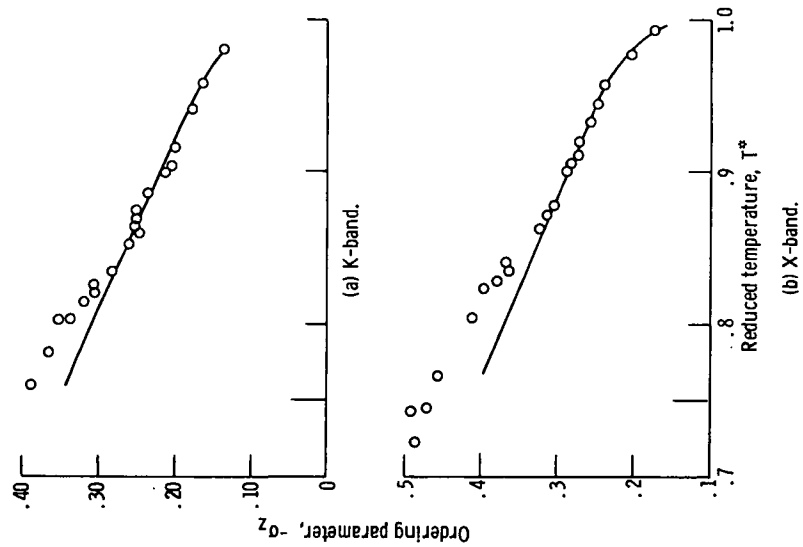Figure 1. - Nitroxide probes used in this study and their structures.

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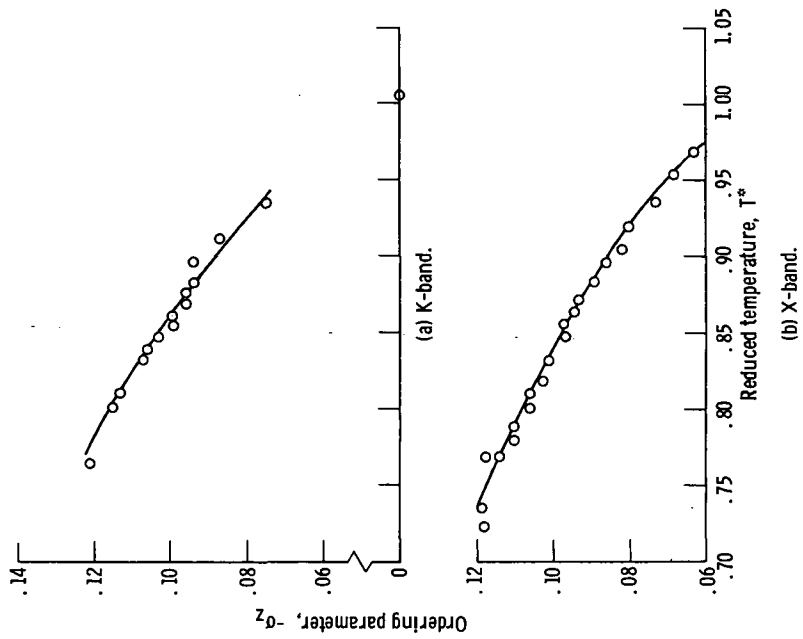Figure 3. – Order parameter of nitroxide 3 in BOCP as function of reduced temperature.

(a) K-band.

(b) X-band.

Reduced temperature, T^*

Ordering parameter, $-\sigma_z$

Figure 2. – Apparent order parameter of VAAC in BOCP as function of reduced temperature.

(a) K-band.

(b) X-band.

Reduced temperature, T^*

Ordering parameter, $-\sigma_z$
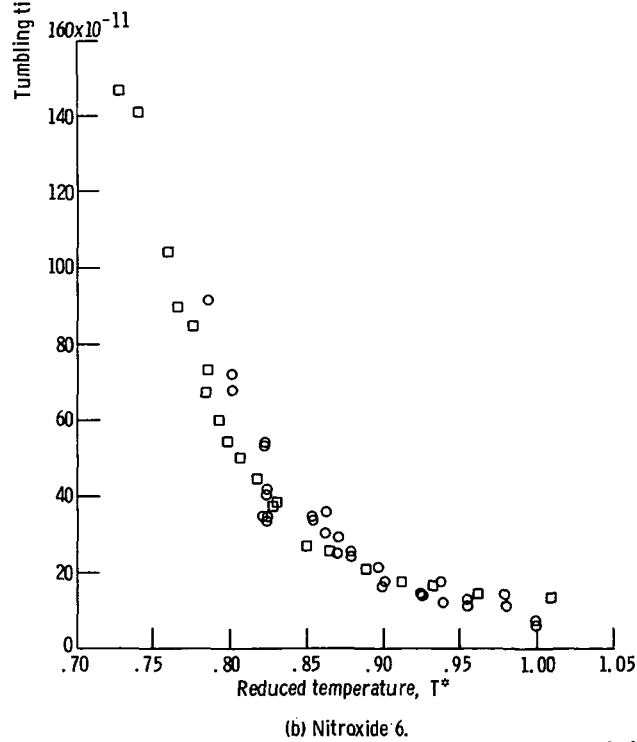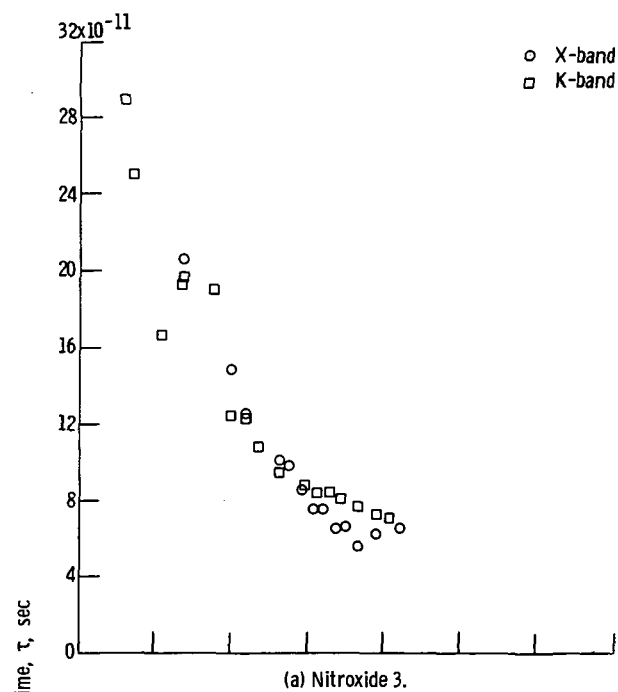
Figure 4. - Tumbling time in BOCP versus reduced temperature.

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